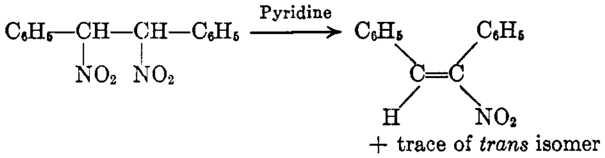

It is clear from a study of models that the isomer with the phenyl groups *cis* allows a closer approach to planarity for the whole molecule and thus the reaction is subject to steric control.

It is interesting to compare the spectra of these nitrostyrene derivatives to those of analogous members of the chalcone and cyanostyrene series. The assignments in the chalcone series[9] are very similar to those made in this study: those compounds exhibiting the longer wave length absorption were assigned the *trans*-chalcone structure. However, in the case of cyanostyrene derivatives[10], such as *cis* and *trans*-α-cyanostilbene or *cis* and *trans*-dicyanostilbene, the isomer with the phenyl groups *trans* absorbed at longer wave lengths than the other isomer. This difference points up the need for reference compounds of known stereochemistry upon which to base spectral assignments particularly in complex systems which contain many chromophores.

Because of the complex nature of the compounds involved it is not possible in this brief examination to assign all the absorption bands. However, it is not unreasonable to assume that the lower wavelength absorption exhibited by all these compounds is probably due to a sterically restricted styrene chromophore. It is interesting, although probably coincidental, that the spectrum of *cis*-α-nitrostilbene is very similar to that of β-methyl-β-nitrostyrene[2] (λ_{max} 226, 305, ϵ_{max} 10300, 12400).

The spectra of the nitroiodostilbenes resemble very closely those of the dinitrostilbenes as might be expected from the similarity of the steric situation. The iodo compounds are probably subject to more steric strains as the *cis*-compound showed only end absorption with no definite peaks or shoulders. The chloro- and iodonitrostyrenes were included for comparative purposes. While both show absorption around 245 mμ and 284 mμ, α-iodo-β-nitrostyrene shows additional absorption at 310 mμ and its absorption is more intense at all three wave lengths. The *trans*-nitrostyrene structure is favored as models indicate a *cis*-nitrostyrene structure is much more sterically crowded.

EXPERIMENTAL[11]

cis and trans-α,α'-Dinitrostilbene. These compounds were prepared and purified by the method previously described.[4]

α-Chloro-trans-β-nitrostyrene. This material was prepared by the addition of nitryl chloride to phenylacetylene and purified as described[12] immediately before measuring the spectrum.

cis- and trans-α-Nitrostilbenes. A mixture containing 25 ml. of benzene, 15 ml. of dioxane, 1 ml. of pyridine, and 1 g. of 1,2-dinitro-1,2-diphenlyethane,[13] m.p. 230–232°, was refluxed for 2 hr. The solution was cooled and washed with dilute hydrochloric acid and water. The residue obtained on removal of the solvent was recrystallized twice from ligroin to give *cis*-α-nitrostilbene as yellow needles, m.p. 74–75°. The filtrates from the recrystallizations were allowed to evaporate slowly, and a mixture of needles and prisms was obtained. Mechanical separation of the small amount of yellow prisms and recrystallization of these from ligroin gave *trans*-α-nitrostilbene, m.p. 127–128°. When the 1,2-dinitro-1,2-diphenylethane, m.p. 149–151°[13] was treated in a similar manner, *cis*-α-nitrostilbene containing a trace of the *trans*-isomer was obtained also.

cis-α-Nitro-α'-iodostilbene, m.p. 113–114°, was obtained in 16% yield from the reaction of tolane and dinitrogen tetroxide in the presence of iodine.[14] Complete details of this reaction will be reported in a future communication.

trans-α-Nitro-α'-iodostilbene, m.p. 176–177°, was obtained in 67% yield from the tolane–dinitrogen tetroxide-iodine reaction.[14]

α-Iodo-β-nitrostyrene, m.p. 50–51°, was obtained from the styrene–dinitrogen tetroxide-iodine reaction.[14]

Spectra. All the samples were measured on a Beckmann DK-1 recording ultraviolet spectrophotometer in absolute alcohol solution.

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(9) W. B. Black and R. E. Lutz, *J. Am. Chem. Soc.*, **75**, 5990 (1953).

(10) D. G. Coe, W. W. Gale, R. P. Linstead, and C. J. Timmons, *J. Chem. Soc.*, 123 (1957); J. F. Codington and E. Mosettig, *J. Org. Chem.*, **17**, 1027 (1952).

(11) We are indebted to Mr. R. D. Strahm for measurement of the spectra.

(12) J. P. Freeman and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 1712 (1957).

(13) J. Schmidt, *Ber.*, **34**, 3536 (1901).

(14) T. E. Stevens and W. D. Emmons, Abstracts, 131st National AMERICAN CHEMICAL SOCIETY Meeting, Miami, Fla., April 1957, p. 11-O.

Improved Synthesis of Monofluoro- and Monochloropyruvic Acids[1]

P. V. NAIR AND HARRIS BUSCH

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Monofluoro- and monochloropyruvic acids have been obtained in yields of 80 and 28 per cent respectively in a highly pure form by hydrolysis and "ketonic fission" of the diethyl esters of the corresponding halo-oxaloacetic acids. The critical conditions for the "ketonic fission" are described and an inverse relationship is indicated between the enol content of the ester and the extent of "ketonic fission".

In connection with the interest of this laboratory in inhibitors of lactic dehydrogenase,[2,3] it became desirable to have a method for the practical

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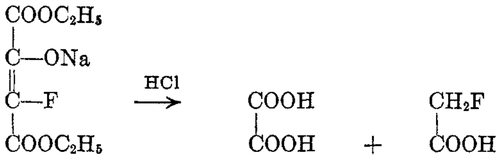
(1) These studies were aided by grants from the U. S. P. H. S. (CY-2886C) and the Jane Coffin Childs Fund.

(2) H. Busch, *Fed. Proc.*, **15**, 229 (1956).

(3) H. Busch and P. V. Nair, *J. Biol. Chem.*, **229**, 357 (1957).

and inexpensive synthesis of fluoropyruvic acid in relatively large amounts. Fluoropyruvic acid was first synthesized by Blank, Mager, and Bergmann.[4–6] The method of Blank *et al.*[6] consisted of the Claisen condensation of ethyl fluoroacetate with diethyl oxalate in the presence of alcohol free sodium ethoxide and the subsequent hydrolysis and decarboxylation of the resulting diethyl sodiofluoro-oxaloacetate by heating with dilute hydrochloric acid at 130° for 6 hours. The solution was concentrated *in vacuo* and extracted with ether. The ether residue was fractionally distilled and fluoropyruvic acid was obtained as a colorless liquid (b.p. 98°/5 mm.), which solidified to a cream-white solid. Blank *et al.*[6] reported a yield of 9 per cent; however, the yield obtained in this laboratory ranged from 0.5 to 2 per cent in eight trials. The product was contaminated with other compounds, including oxalic acid, which was difficult to remove.

In the present studies it was found that the yield and purity of fluoropyruvic acid could be substantially improved by initially isolating the free ester, diethyl fluoro-oxaloacetate,[7] from the enolate and then effecting the hydrolytic "ketonic fission" of the free ester. With the free ester as the starting material, the yield of fluoropyruvic acid was 80 per cent of the theoretical yield. The product melted sharply at 85–86° and contained no oxalic acid. The present experiments have confirmed the findings of Blank *et al.*[6] who reported that oxalic and fluoroacetic acid were the major products of the hydrolytic scission of diethyl sodiofluoro-oxaloacetate. This result indicates that the predominant reaction in the hydrolysis of the enolate is the "acid fission,"



$$\mathrm{C_2H_5OOC{-}C(ONa){=}C(F){-}COOC_2H_5} \xrightarrow{\mathrm{HCl}} \mathrm{HOOC{-}COOH} + \mathrm{CH_2F{-}COOH}$$

as contrasted to the "ketonic fission" of the free ester.

This apparent relationship of the enol content of the starting material to the yield of fluoropyruvic acid suggested that enol content might be related to the extent of "ketonic fission" of esters of oxaloacetic acid and its halo derivatives. Therefore these studies were extended to the diethyl esters of oxaloacetic acid and chloro-oxaloacetic acid whose enol content has been reported (Table 1). Diethyl oxaloacetate was prepared from the commercially available sodium salt and diethyl chloro-oxaloacetate by the method of Wislicenus.[8] Table I presents a comparison of the yield of the corresponding pyruvic acid and the enol content of the ester.

TABLE I

Compound	Yield of keto acid based on the ester, %	Enol content,[8] %
Diethyl oxaloate	5–9	72–79
Diethyl chloro-oxaloacetate	(a) 32–33 (b) 25	24–27
Diethyl fluoro-oxaloacetate	80	8–9

These data indicate an inverse relationship between the enol content and the extent of "ketonic fission" in these series of compounds. The low yield of fluoropyruvic acid obtained under the experimental conditions of Blank *et al.*[6] may be explained by this relationship.[9]

An interesting by-product of these studies was the unequivocal synthesis of monochloropyruvic acid by the "ketonic fission" of diethyl chloro-oxaloacetate. The earlier method[10] reported in the literature for the preparation of this compound (from pyruvic acid and sulfuryl chloride) yields a product contaminated with dichloropyruvic acid, which is difficult to remove.

EXPERIMENTAL[11]

Diethyl fluorooxaloacetate. The enolate was prepared by the method of Blank *et al.*[6,12] (yield, 79–80%). The free ester was obtained by a procedure similar to that of Rivett.[7] The enolate (114 g., 0.5 mole) was washed with anhydrous ether until the washings were colorless, suspended in ether (200 ml.), and cooled to −20°. Then 5*N* hydrochloric acid[13] (100 ml.) cooled to −20° was rapidly added to the ethereal suspension and shaken well. The ether layer was separated, and the mixture was extracted with two 50-ml. portions of ether. The combined ether extracts were washed with cold water, dried (Na_2SO_4), and the solvent was removed. Distillation of the residue yielded diethyl fluoro-oxaloacetate as a pale yellow liquid (51 g., 50%), b.p. 98–100°/1.1 mm. (Rivett[7] reported b.p. 99°/3 mm.; Blank *et al.*[6] reported b.p. 120–122°/9 mm.). Melting point of the *2,4-dinitrophenylhydrazone*, 123–124° (Blank and Mager,[5] report m.p. 124°).

Fluoropyruvic acid. Diethyl fluorooxaloacetate (41.2 g., 0.2 mole) was refluxed with 3*N* hydrochloric acid (300 ml.) at 105° for 1 hr. After standing overnight, the solution was concentrated *in vacuo* to a very low volume at 40–45°/5 mm. The residue was fractionated and fluoropyruvic acid condensed as a white solid in the condenser[14] and the

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(4) J. Mager and I. Blank, *Nature*, **173**, 126 (1954).

(5) I. Blank and J. Mager, *Experientia*, **10**, 77 (1954).

(6) I. Blank, J. Mager, and E. D. Bergmann, *J. Chem. Soc.*, 2190 (1955).

(7) D. E. A. Rivett, *J. Chem. Soc.*, 3710 (1953).

(8) W. Wislicenus, *Ber.*, **43**, 3528 (1910).

(9) The conversion of the sodium enolate to the keto form may be in competition with the "acid fission" of the enolate under the conditions of Blank *et al.*

(10) M. Garino and I. Muzio, *Gazz. chim. ital.*, **52**, 227 (1926).

(11) Analyses are by the Clark Microanalytical Laboratory, Urbana, Ill., and Drs. Weiler and Strauss, Oxford, England. Melting and boiling points are uncorrected.

(12) For the preparation of fluoropyruvic acid it was found that sodium methoxide (from commercial sources) could be substituted for sodium ethoxide.

(13) This can be replaced by *N* hydrochloric acid.

(14) It is advisable to disconnect the condenser from the water tap as soon as the fluoropyruvic acid begins to distill over and solidify. Hot water may be circulated through the condenser at this stage.

Claisen head from which the solid was removed with a glass spatula, yield 17 g. (80%). It was free of oxalic acid as shown by the absence of the color reaction with diphenylamine.[15] The product was purified by sublimation *in vacuo* (at 70–80°/0.5–0.7 mm.) and obtained as a fine white crystalline powder. The m.p. of the product was 86° immediately after drying *in vacuo* over P_2O_5. The product is very hygroscopic.

Semicarbazone (recrystallized from 95% alcohol) turns brown at 198–200° and decomposes at 205°.

Anal. Calcd. for $C_4H_6N_3N_3F$: C, 29.45; H, 3.7; N, 25.7. Found: C, 29.8; H, 3.43; N, 25.17%.

Dinitrophenylhydrazone[16] (crystallized 4 times from alcohol) begins to melt at 163° and decomposes at 165°.

Anal. Calcd. for $C_9H_7N_4O_6F$: C, 37.77; H, 2.47; N, 19.58. Found: C, 37.8; H, 2.66; N, 19.8%.

Diethyl chlorooxaloacetate. This compound was prepared by the method of Wislicenus.[8] Light yellow liquid, b.p. 114°/1.4 mm., yield, 53% (Wislicenus reported a yield of 28%, b.p. 150–152°/56 mm.).

Monochloropyruvic acid. A procedure similar to that described for the preparation of monofluoropyruvic acid was followed to obtain this compound. Diethyl chlorooxaloacetate (22.25 g., 0.1 mole) yielded 3 g. (25%) of chloropyruvic acid (distilled at 92°/3 mm. and solidified to a white solid in the condenser).

The product was purified by sublimation *in vacuo* (70°/0.1 mm.) and dried *in vacuo* over P_2O_5, m.p., 83–84° (Garino and Muzio,[10] m.p., 45°; product + H_2O, m.p., 55°). Neutral equivalent, found: 122.9 (theory, 122.5). *Dinitrophenylhydrazone* (recrystallized from alcohol) melted at 167–168°.

Anal. Calcd. for $C_9H_7N_4O_6Cl$: C, 35.71; H, 2.33; N, 18.51; Cl, 11.72. Found: C, 35.94; H, 2.67; N, 18.55; Cl, 11.78%.

Diethyl oxaloacetate was obtained from the commercially available sodium salt of the ester, as in the case of the fluoro derivative, as a clear colorless liquid, b.p. 96–97°/2.5 mm., yield 64%.

Pyruvic acid. Diethyl oxaloacetate (18.8 g., 0.1 mole) was hydrolyzed under the same conditions as in the case of the fluoro derivative, 0.5–1 g. (5–9%) of pyruvic acid was obtained. The product distilled at 40°/2 mm.; a specimen of pure pyruvic acid distilled at 40°/3.5 mm. *Phenylhydrazone* (crystallized from alcohol), m.p. 193° (Fischer,[17] m.p. 192°); mixed m.p. with an authentic specimen of the phenylhydrazone of pyruvic acid, 192–193°.

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[15] F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., Inc., New York, 1956.

[16] In comparing the melting points of the dinitrophenylhydrazones the *cis-trans* isomerism that is possible in these compounds must be taken into consideration.

[17] E. Fischer, *Ber.*, **17**, 578 (1884).

Thermal Rearrangement of Hexamethyldisilane to Trimethyl(dimethylsilylmethyl)silane

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During the course of a recent investigation of the organo-substituted disilanes we have found that hexamethyldisilane (I) readily undergoes rearrangement at 600° to give trimethyl(dimethylsilylmethyl)silane (II). At 400°, no thermal reaction of I occurred.

$$\underset{\text{I}}{(CH_3)_3SiSi(CH_3)_3} \xrightarrow{600°} \underset{\text{II}}{(CH_3)_3SiCH_2Si(CH_3)_2H}$$

It has been found in this laboratory[1] that chloromethyldisilane derivatives such as $ClCH_2(CH_3)_2SiSi(CH_3)_3$ and $ClCH_2(CH_3)_2SiSi(CH_3)_2Cl$ rearrange in the presence of aluminum chloride to the corresponding disilylmethane, *i.e.*, $(CH_3)_3SiCH_2Si(CH_3)_2Cl$ and $Cl(CH_3)_2SiCH_2Si(CH_3)_2Cl$, respectively. The present reaction may be described tentatively in terms of the following scheme:

$$(CH_3)_3SiSi(CH_3)_3 \xrightarrow{600°} 2\ (CH_3)_3\dot{S}i$$

$$(CH_3)_3\dot{S}i + (CH_3)_3SiSi(CH_3)_3 \longrightarrow (CH_3)_3SiH + (CH_3)_3SiSi(CH_3)_2CH$$

$$(CH_3)_3SiSi(CH_3)_2CH_2 \longrightarrow (CH_3)_3SiCH_2\dot{S}i(CH_3)_2$$

$$(CH_3)_3SiCH_2\dot{S}i(CH_3)_2 + (CH_3)_3SiSi(CH_3)_3 \longrightarrow (CH_3)_3SiCH_2Si(CH_3)_2H + (CH_3)_3SiSi(CH_3)_2\dot{C}H_2$$

EXPERIMENTAL[2]

Hexamethyldisilane (40 g., 0.27 mole) was passed slowly through a 4.0 × 100 cm. quartz tube heated to 600°. Fractional distillation in 1.0 × 30 cm. Stedman column of the product gave 33 g. of a mixture of I and II ,boiling over the range 112–120°, in addition to 2 g. of very volatile matter which was believed to be trimethylsilane.

A sample of the former distillate, b.p. 120°, n_D^{20} 1.4122, d_4^{20} 0.7462 (reported[3] for compound II: b.p. 119–121°, n_D^{20} 1.4158, d_4^{20} 0.7454) was analyzed for silane hydrogen in the Zerewitinoff apparatus using sodium *n*-butoxide in *n*-butyl alcohol as alkaline reagent. Ninety-three per cent of the theoretical quantity of hydrogen was evolved. Under these conditions compound I is quite stable to cleavage.

Further proof of II was afforded by treatment of the distillate (30 g.) with ethanolic solution of sodium ethoxide at 60°. Fractionation of the reaction mixture was made after complete evolution of hydrogen to give 7.2 g. of unchanged hexamethyldisilane and 12 g. of trimethyl(dimethylethoxysilylmethyl)silane, b.p. 159°, n_D^{20} 1.4183 (reported[3] b.p. 161–161.5°, n_D^{20} 1.4169).

Anal. Calcd. for $C_8H_{22}OSi_2$: Si, 29.5. Found: Si, 29.5, 29.3.

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[1] M. Kumada, J. Nakajima, M. Ishikawa, and Y. Yamamoto, *J. Org. Chem.*, in press.

[2] Boiling points are uncorrected.

[3] A. V. Topchier, N. S. Nametkin, and L. S. Povarov, *Doklady Akad. Nauk S.S.S.R.*, **97**, 99 (1954); *Chem. Abstr.*, **49**, 8792 (1955).